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The crystal structure of β-RDX – an elusive form of an explosive revealed**

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Supporting information:
[†] CCDC 705290 and 705291. For crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/B817966B

Graphical abstract:

Abstract

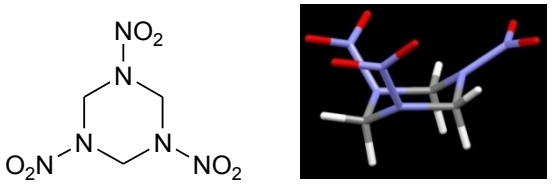
The crystal structure of the highly metastable β-form of RDX shows that the molecules adopt different conformations compared to the α-form and that, contrary to previous reports, the β-form obtained at ambient pressure is not the same form as that obtained at elevated temperatures and pressures.

Main text

The performance of energetic materials (propellants and explosives) depends on several factors that include crystal density, detonation velocity, and sensitivity to detonation by stimulus.[1] These in turn are governed by the solid-state structure of the energetic material. In order to model and understand the characteristics and performance of these materials, it is essential to obtain detailed structural information over a range of conditions of temperature and pressure. This information can be used to explore aspects of energetic materials that include: sensitivity to shock, heat, and friction; chemical decomposition mechanisms; energy transfer through the solid; detonation velocities; the efficacy of theoretical modelling techniques.

RDX (1,3,5-trinitrohexahydro-1,3,5-triazine) is a widely used military explosive that can be compounded with mineral jelly or polymers to form plastic explosives such as C4 and PBX compositions. To date, two polymorphic forms have been structurally characterised. The structure of the orthorhombic α-form (space group *Pbca*) has been determined by both single crystal X-ray[2] and neutron diffraction[3] and shows that the RDX molecule adopts a chair conformation in which two of the nitro-groups are in pseudo-axial positions and the other is in a pseudo-equatorial position – this is denoted as the AAE conformation (see Figure 1). Compression of the α-form to pressures > 3.9 GPa at ambient temperature gives the γ-form,[4] and this was recently structurally characterised by single crystal X-ray and neutron powder diffraction.[5] The two independent molecules in the asymmetric unit of this structure adopt different conformations which are best described as AAA and AAI, respectively, where I denotes an intermediate orientation of the NO_2 group midway between axial and equatorial positions.[5] Recent spectroscopic studies have also suggested a further high-pressure form obtained above 17.8 GPa at ambient temperature, which has been denoted the δ-form.[6,7]

A highly metastable β-form was first reported in 1950 by crystallisation from high boiling solvents such as thymol and nitrobenzene, but on account of its instability with respect to the α-form it was not possible to obtain and preserve well-formed crystals.[8] Subsequent IR spectroscopic studies of β-RDX have suggested that the RDX molecules adopt essentially C_{3v} symmetry, on the basis of fewer bands observed in the IR spectrum for β-RDX compared to α-RDX.[9,10,11] Each of these studies concluded that all of the nitro-groups are equivalent and similar to the proposed AAA conformation adopted in the solution[9,10,11] and vapour phases.[12] However, the ease of conversion from β-RDX to α-RDX has hampered all subsequent attempts to characterise this form.



(a) **(b)**

Figure 1. (a) Molecular structure of RDX; (b) The AAE conformation adopted by α-RDX.

Two spectroscopic studies of RDX at high temperatures and pressures have also suggested the presence of another form of RDX. Baer *et al*. observed a transition to a new form at pressures >3.8 GPa and a temperature of 375 K using liquid nitrogen as a pressure-transmitting medium.[13] A later study by Miller *et al*. using Fluorinert as a pressure-transmitting medium also observed a transition at similar pressures, but at a higher temperature (488 K).[4], Due to similarities in vibrational spectra and the observation that this form persisted on decompression at ambient temperature almost to ambient pressure, both studies concluded that this high-temperature high-pressure form is the β-form.

As part of our wider programme to explore the effects of pressure on the structures of energetic materials we have chosen to investigate the structural relationships between the various forms of RDX as a function of both pressure and temperature. In particular, we wished to shed light on the elusive β-form, both under ambient conditions and at elevated pressures and temperatures.

Initial experiments focused on crystallisation of RDX from nitrobenzene solution in sealed glass capillaries (o.d. ~2 mm). By thorough warming of this sealed system (~420 K), to ensure that *all* of the solid had dissolved, it was possible to reduce the likelihood of seeding by residual traces of the α-form. In this way, reproducible crystallisation conditions were achieved and upon cooling a very concentrated hot solution to 298 K small crystallites were obtained which exhibited a very different morphology from α-RDX. Raman spectroscopy identified these as the β-form by comparison with previously reported spectra.[11] A single crystal was successfully grown using this same technique in a smaller diameter capillary (~0.3 mm) and single crystal X-ray diffraction data were recorded at 273 K. Structure solution and refinement showed that this was an unsolvated form of RDX, space group $Pca2_1$, with $Z' = 2$. Attempts to cool the capillary resulted in freezing of the nitrobenzene and destruction of the crystal. Subsequent crystallisation trials focussed on growing single crystals that could be separated from the solvent so that higher quality low-temperature data could be collected. The most successful route proved to be when a concentrated solution on a hot glass slide was covered with an upturned glass vial to reduce the evaporation rate. In the cases where the drop contacted the side of the upturned vial, small dendritic crystals of β-RDX were observed to form at the meniscus during evaporation. This method is very similar to the phenomenon of "contact-line crystallisation" described by

Capes *et al.* for the growth of a metastable polymorph of paracetamol.[14] Crystals grown in this way proved to be sufficiently metastable with respect to the α-form that they could be manipulated and transferred to a fibre which was subsequently mounted on the diffractometer. In this way, single crystal X-ray diffraction data were recorded at 150 K which were found to be consistent with the data collected at 273 K.

In the crystal structure of the β-form, both independent molecules adopt the chair conformation with all nitro groups in axial positions, resulting in approximate C_{3v} molecular symmetry (see Figure 2), thus supporting earlier suggestions based on vibrational spectra.[10,11]

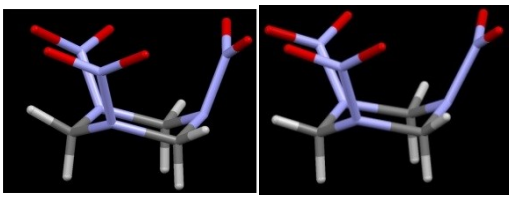


Figure 2. Conformations of the two independent molecules in β-RDX.

The orientations of the nitro-groups can conveniently be compared by reference to the angle δ, which is defined as the angle between the plane of the C-N-C ring atoms and the corresponding N-N bond.[12] The δ-values for both molecules in β-RDX are presented in Table 1 alongside those for α-RDX and for the *isolated* molecule in the AAA conformation as calculated using DFT methods.[15] For both molecules 1 and 2 the δ-values are very close to the calculated AAA geometry.

Table 1. Values of δ (in °) for different conformations of RDX

α-form	**β-form (molecule 1)**	**β-form (molecule 2)**	**AAA**[a]
33.4	28.9	27.8	30.3
33.9	31.4	28.7	30.1
-19.8	39.0	32.1	29.9

[a] calculated from ref. 15

A particularly striking aspect of the crystal structure is the unusually large anisotropic displacement parameters (illustrated in Figure 3) associated with the nitro-groups and ring atoms of molecule 1. These large amplitude motions (even at 150 K) suggest that molecule 1 is librating significantly about its position in the lattice and it is perhaps this motion that is a factor in the ease of the β → α transformation.

The packing of the molecules can be described as two interpenetrating lattices, one of which is composed solely of type 1 molecules and the other composed solely of type 2 molecules (see Figures 4a and 4b). Weak

C-H…O intermolecular interactions link molecules within each these lattices. These interactions are also present between molecules 1 and 2 in the full lattice (see Fig 4c). This arrangement results in a slightly less dense structure (1.795 g cm^{-3} at 273 K) compared to α-RDX (1.806 g cm^{-3} at 293 K).[3] Comparison of the α- and β-forms shows that there is no direct relationship between the structures and that the β-form exhibits fewer C-H…O intermolecular interactions.

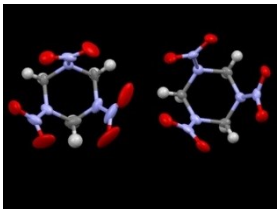


Figure 3. Thermal ellipsoids for molecules 1 and 2.

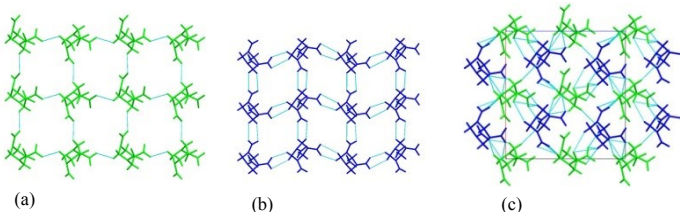


Figure 4. (a) Lattice composed of type 1 molecules (green) (viewed down the *b*-axis); (b) lattice composed of type 2 molecules (blue); and (c) the two interpenetrating lattices. In all cases, the C-H…O intermolecular contacts are shown.

The results of these studies indicate that the β-form is rather less prone to transform to the α-form than previously suggested.[8] Thus crystals of β-RDX may be manipulated at ambient temperature both in the presence of solution and when dry provided that there are no traces of the α-form. In the presence of the α-form, solvent mediated transformation is very rapid. Likewise, an isolated crystal of the β-form immediately transformed on contact with a fibre or needle contaminated with a trace of the α-form. In this case a wavefront was observed to pass through the crystal leading to a very marked deterioration in crystal quality, indicating that the transition is reconstructive. As has been suggested in earlier studies,[10] this instability would exclude the possibility of the presence of the β-form in RDX-containing compositions. Hence this would rule out any direct effects of the β-form on the performance of these compositions (e.g. sensitivity to shock) although it is of course possible that the β → α transition might affect crystal quality through the introduction of shear stresses and/or crystal defects with implications for the creation of "hot-spots", thereby potentially affecting performance. Thus we are currently investigating the effects of the phase history of samples of RDX on their sensitivity to initiation.

We also investigated the high-pressure, high-temperature form, which has also been labelled the β-form,[4,13] using neutron powder diffraction. On warming a sample of RDX-d_6 to 500 K at a pressure of 5.5 GPa, a new diffraction pattern was obtained that was substantially different from patterns previously obtained for the α- and γ-forms.[5] This pattern persisted on decompression at ambient temperature to a pressure of ~1.0 GPa, and then at lower pressures reverted to the α-form. This showed that the sample had *not* decomposed under the elevated conditions of pressure and temperature, and this was subsequently corroborated by analysis of the recovered sample by Raman spectroscopy and X-ray powder diffraction. The new pattern was also significantly different (less complex) from the pattern calculated from the crystal structure of the β-form, even accounting for the effects of pressure on the lattice parameters. Instead, our neutron diffraction data represent a new high-pressure/high-temperature form which is clearly *not* the β-form obtained at ambient pressure.

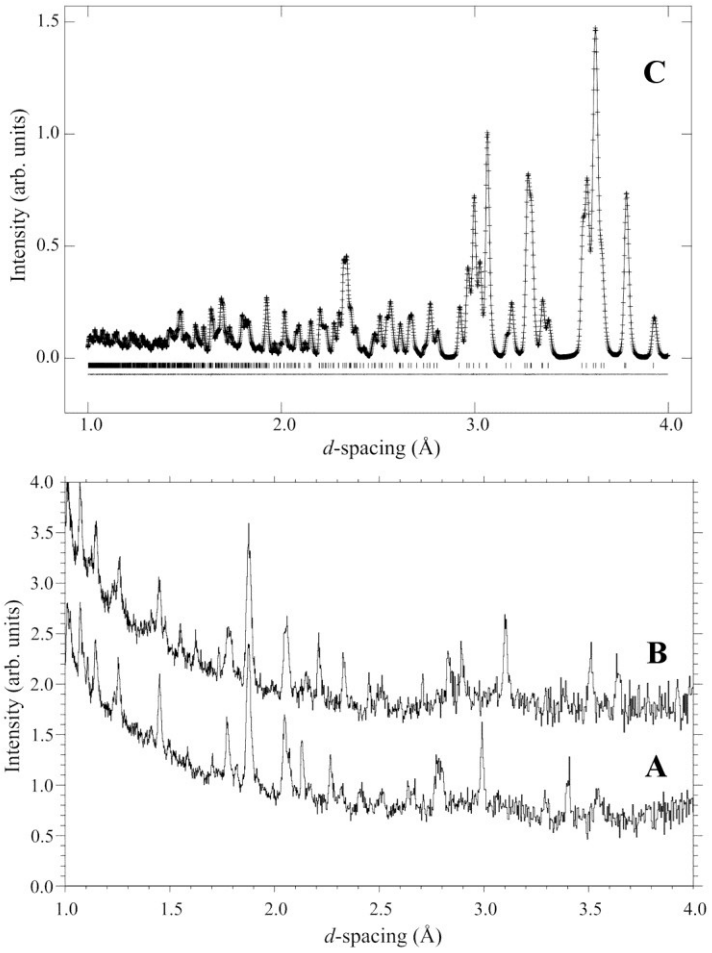


Figure 5. Comparison of neutron powder diffraction patterns obtained for a sample of RDX-d_6 subjected to elevated pressures and temperatures (**A**: ~5.5 GPa and 373 K; **B**: ~1.0 GPa and 293 K) with the simulated pattern for perdeuterated β-RDX (**C**).

Conclusions

The crystal structure of the highly metastable β-form of RDX has been determined. This is a significant achievement given McCrone's comment that *"because of its physical instability, there is no possibility of obtaining (this form) even in laboratory recrystallizations.*[8]*"* Although β-RDX is very prone to transform to the more stable α-form and hence is unlikely to be found in RDX-containing compositions, the reconstructive nature of the transformation may have implications for the sensitivity and performance of munitions. Furthermore, contrary to accepted wisdom, we have established that the β-form obtained at ambient pressure is not the same form as that obtained at elevated temperatures and pressures. Thus we suggest that the high-temperature, high-pressure form previously identified as the β-form should now be re-named as the ε-form.

Notes and references

[‡] Crystalline samples of RDX (SME type II; 100–300 μm) were kindly provided by W.G. Proud (Cavendish Laboratory, University of Cambridge). X-ray diffraction intensities were collected using Mo-Kα radiation on a Bruker SMART APEX CCD diffractometer[16] equipped with an Oxford Cryostream-*Plus* low-temperature device.[17] Structures were solved[18] and refined by full-matrix least squares against F^2 using all data.[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically placed on the parent carbon. X-ray data: β-phase $C_3H_6N_6O_6$ M = 222.12, orthorhombic, space group $Pca2_1$, a = 15.1267 (11), b = 7.4563 (6), c = 14.3719 (11) Å, V = 1621.0 (2) Å^3, T = 150 K, Z = 8, μ = 0.173 mm^{-1}, D_c = 1.820 Mg m^{-3}, λ = 0.71073 Å, θ_{max} = 28.425°, 10899 reflections measured, 2097 unique (R_{int} = 0.038). R_1 = 0.0465, wR_2 = 0.0847 for all 2097 data; a = 15.0972(7), b = 7.5463(4), c = 14.4316(6) Å, V = 1644.16(13) Å^3, T = 273(2) K, Z = 8, μ(Mo-Kα) = 0.171 mm^2, Dc = 1.795 Mg/m^3, λ = 0.71073 Å, θmax = 23.312°, 10137 reflections measured, 1244 unique (*Rint* = 0.055). Final residuals for 271 parameters were *R1* = 0.0525, *wR2* = 0.1292 for $I > 2\sigma(I)$, and *R1* = 0.0975, *wR2* = 0.1405 for all data. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/ or CCDC reference number 705291. For neutron powder diffraction experiments a lightly ground sample (*ca.* 100 mg) of RDX-d_6 (prepared by nitration of hexamine-d_{12})[20] was loaded into an encapsulated TiZr gasket together with a small quantity of 4 : 1 perdeuterated methanol-ethanol as pressure-transmitting medium and a small quantity of lead as pressure calibrant. The capsule was then compressed within a type V3b Paris-Edinburgh (P-E) press fitted with a compact variable-temperature insert which permits cooling or heating of just the anvil and gasket assembly.[21] High-pressure neutron powder diffraction data were collected using the PEARL/HiPr diffractometer at the UK spallation neutron source, ISIS, located at the STFC Rutherford Appleton Laboratory.

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